

WHAT IS CLAIMED IS:

1. A cathode material for a rechargeable electrochemical cell, said cell also comprising an anode and an electrolyte, the cathode material comprising a compound having the formula LiMPO_4 , where M is at least one first-row transition-metal cation.
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2. The cathode material of claim 1, where M is further defined as being selected from the group consisting of Mn, Fe, Co, and Ni
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3. The cathode material of claim 1, where M is further defined as being a combination of cations, at least one of which is selected from the group consisting of Mn, Fe, Co and Ni.
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4. The cathode material of claim 3, where M is $\text{Fe}_{1-x}\text{Mn}_x$ or $\text{Fe}_{1-x}\text{Ti}_x$ and $0 < x < 1$.
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5. The cathode material of claim 2, wherein the cathode material has the formula LiFePO_4 .
6. A cathode material for a rechargeable electrochemical cell, said cell also comprising an anode and an electrolyte, the cathode material comprising a rhombohedral NASICON material having the formula $\text{Y}_x\text{M}_2(\text{PO}_4)_3$, where M is at least one first-row transition-metal cation and $0 \leq x \leq 5$ and Y is Li or Na.
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7. The cathode material of claim 5, where M is selected from the group consisting of Fe, V, Mn, and Ti.
8. The cathode material of claim 7, wherein the cathode material has the formula $\text{Li}_{3+x}\text{Fe}_2(\text{PO}_4)_3$, where $0 \leq x \leq 2$.
9. The cathode material of claim 7, wherein the cathode material has the formula $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$.

10. The cathode material of claim 7, having the formula $\text{Li}_{1+x}\text{Ti}_2(\text{PO}_4)_3$.

11. The cathode material of claim 7, having the formula $\text{Li}_2\text{FeTi}(\text{PO}_4)_3$.

5 12. The cathode material of claim 7, having the formula $\text{Li}_x\text{TiNb}(\text{PO}_4)_3$, where $0 \leq x \leq 2$.

13. The cathode material of claim 7, having the formula $\text{Li}_{1+x}\text{FeNb}(\text{PO}_4)_3$, where $0 \leq x \leq 2$.

14. The cathode material of claim 7, prepared by the process comprising the steps:

- 10 (a) preparing $\text{Na}_2\text{Fe}_2(\text{PO}_4)_3$; and
(b) contacting said $\text{Na}_2\text{Fe}_2(\text{PO}_4)_3$ with a molten lithium salt, such that an ionic exchange reaction occurs.

15 15. The cathode material of claim 7, prepared by a direct solid state reaction.

16. A cathode material for a rechargeable electrochemical cell, said cell also comprising an anode and an electrolyte, the cathode material comprising a rhombohedral NASICON material having the formula $\text{Y}_x\text{M}_2(\text{PO}_4)_y(\text{XO}_4)_{3-y}$, where $0 < y \leq 3$, M is a transition-metal atom, $0 \leq x \leq 5$, Y is Li or Na, and X = Si, As, or S.

20 17. The cathode material of claim 16, wherein the cathode material has the formula $\text{Li}_{1+x}\text{Fe}_2(\text{SO}_4)_2(\text{PO}_4)$, where $0 \leq x \leq 2$.

18. The cathode material of claim 17, prepared by the process comprising the steps:

- 25 (a) preparing an aqueous solution comprising FeCl_3 , $(\text{NH}_4)_2\text{SO}_4$, and LiH_2PO_4 ;
(b) evaporating the solution to obtain dry material; and
(c) heating the dry material to about 500°C .

19. A cathode material for a rechargeable electrochemical cell also comprising an anode and an electrolyte, the cathode comprising a rhombohedral NASICON material having the formula $A_{3-x}V_2(PO_4)_3$, where A may be Li, Na or a combination thereof and $0 \leq x \leq 2$.

5 20. The cathode material of claim 19, wherein the cathode material has the formula Li_2
 $_xNaV_2(PO_4)_3$, where $0 \leq x \leq 2$.

10 21. The cathode material of claim 19, prepared by the process comprising the steps:

- (a) preparing $Na_3V_2(PO_4)_3$; and
- 10 (b) contacting said $Na_3V_2(PO_4)_3$ with a molten lithium salt, such that an ionic exchange reaction occurs.

15 22. The cathode material of claim 19, prepared by a direct solid-state reaction.

15 23. A cathode material for a rechargeable electrochemical cell, said cell also comprising an anode and an electrolyte, the cathode material comprising a compound having the formula:



where

20 M may be Fe^{2+} or Mn^{2+} or mixtures thereof;

D is a metal in the +2 oxidation state selected from the group consisting of:

Mg^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cu^{2+} and Ti^{2+} ;

T is a metal in the +3 oxidation state selected from the group consisting of:

Al^{3+} , Ti^{3+} , Cr^{3+} , Fe^{3+} , Mn^{3+} , Ga^{3+} , Zn^{2+} , and V^{3+} ;

25 Q is a metal in the +4 oxidation state selected from the group consisting of:
 Ti^{4+} , Ge^{4+} , Sn^{4+} , and V^{4+} ;

R is a metal in the +5 oxidation state selected from the group consisting of:
 V^{5+} , Nb^{5+} , and Ta^{5+} ;

$0 \leq x \leq 1$;

$0 \leq y, d, t, q, r, p, s, v \leq 1$ where at least one of y, d, t, q, r, p, s, and v differ from 0 and

$$y + d + t + q + r \leq 1;$$

$$p + s + v \leq 1; \text{ and}$$

$$3 + s - p = x - y + t + 2q + 3r;$$

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where x is the degree of intercalation during operation of the electrode material, y represents the fraction of lithium ions on the initial Fe^{2+} sites; d represents the fraction of divalent ions (noted as D) on the initial Fe^{2+} sites; t represents the fraction of trivalent ions (noted as T) on the initial Fe^{2+} sites; q represents the fraction of tetravalent ions (noted as Q) on the initial Fe^{2+} sites; r represents the fraction of pentavalent ions (noted as R) on the initial Fe^{2+} sites; p represents the fraction of hexavalent suflur (as discrete SO_4^{2-} tetrahedra) on the initial P^{5+} sites; s represents the fraction of tetravalent silicon (as discrete SiO_4^{2-} tetrahedra) on the initial P^{5+} sites; and v represents the fraction of pentavalent vanadium ions on the initial P^{5+} sites, and M, D, T, Q and R reside in octahedral sites.

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24. A secondary battery comprising an anode, a cathode and an electrolyte, said cathode comprising an ordered olivine compound having the formula LiMPO_4 , where M is at least one first-row transition-metal cation.

25. The battery of claim 23, where M is further defined as being selected from the group consisting of Mn, Fe, Co, and Ni.

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26. The battery of claim 23, where M is further defined as being a combination of cations, at least one of said cations being selected from the group consisting of Mn, Fe, Co, and Ni.

27. The battery of claim 25, wherein M is $\text{Fe}_{1-x}\text{Mn}_x$ or $\text{Fe}_{1-x}\text{Ti}_x$, where $0 \leq x \leq 1$.

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28. A secondary battery comprising an anode, a cathode and an electrolyte, said cathode comprising a modified olivine compound as set forth in claim 23.

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29. The battery of claim 28, wherein the anode comprises a compound selected from the group consisting of a metallic lithium, a lithium alloy, a lithium-carbon intercalation compound, a lithium-transition metal mixed nitride of antifluorite and a lithium-titanium spinel having the formula $\text{Li}_{1+\frac{\alpha}{x}+z}\text{Ti}_{2-\frac{\alpha}{x}}\text{O}_4$ where $0 \leq \frac{\alpha}{x} \leq 1/3$ and $0 \leq z \leq 1 - 2\frac{\alpha}{x}$.

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30. The battery of claim 29, wherein said cathode further comprises a conductive additive.

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31. The battery of claim 30, wherein said conductive additive is carbon.

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32. The battery of claim 29, wherein said cathode further comprises an intercalation material with fast diffusion kinetics.

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33. The battery of claim 32, wherein said intercalation material is selected from the group consisting of a lamellar dichalcogenide, a vanadium oxide having the formula $\text{VO}_{\frac{a}{x}}$ where $2.1 \leq \frac{a}{x} \leq 2.5$, and a NASICON-related material.

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34. The battery of claim 33, wherein said NASICON-related material is selected from the group consisting of $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and $\text{Li}_{3-\frac{a}{x}}\text{Fe}_{2-\frac{a}{x}}\text{Ti}_{\frac{a}{x}}(\text{PO}_4)_3$.

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35. The battery of claim 30, wherein said cathode further comprises a polymeric binder.

36. The battery of claim 35, wherein said polymeric binder is selected from the group consisting of a homopolymer of tetrafluoroethylene, a copolymer of tetrafluoroethylene, an ethylene-propylene-diene terpolymer, a polyether, a polyester, a methylmethacrylate-based polymer, an acrylonitrile-based polymer, and a vinylidene fluoride-based polymer.

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37. The battery of claim 36, wherein said polymeric binder is a polyether.

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38. The battery of claim 37, wherein said polyether further comprises a salt comprising Li⁺ cations.

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39. The battery of claim 38, wherein said polyether is crosslinked.

40. The battery of claim 35, wherein said polymeric binder has an ionic conductivity of between about 10⁻⁷ and about 10⁻² (Scm⁻¹) at room temperature

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41. The battery of claim 38, wherein said polymeric binder is swollen by an aprotic solvent.

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42. The battery of claim 41, wherein said aprotic solvent is selected from the group consisting of: ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, methyl-ethylcarbonate, γ-butyrolactone, a tetraalkylsulfamide, a dialkylether of an ethylene glycol having a molecular weight ≤ 2000.

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43. The battery of claim 42, wherein said aprotic solvent is a dialkylether of an ethylene glycol having a molecular weight ≤ 2000.

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44. The battery of claim 43, wherein said dialkylether comprises a mono-ethylene glycol.

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45. The battery of claim 43, wherein said dialkylether comprises a di-ethylene glycol.

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46. The battery of claim 43, wherein said dialkylether comprises a tri-ethylene glycol.

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47. The battery of claim 43, wherein said dialkylether comprises a tetra-ethylene glycol.

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48. The battery of claim 43, wherein said dialkylether comprises an oligo-ethylene glycol higher than a tetra-ethylene glycol.

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49. The battery of claim 42, wherein said dialkylether comprises a mixture of mono-, di-, tri-, tetra-, and higher oligo-ethylene glycols.

5 50. A secondary battery comprising an anode, a cathode and an electrolyte, said cathode comprising a rhombohedral NASICON material having the formula $Y_xM_2(PO_4)_3$, where M is at least one first-row transition-metal cation and $0 \leq x \leq 5$ and Y is Li or Na, other than $Li_{2+x}FeTi(PO_4)_3$.

10 51. The battery of claim 27, where M is selected from the group consisting of Fe, V, Mn, and Ti.

52. The battery of claim 28, wherein the cathode material has the formula $Li_{3+x}Fe_2(PO_4)_3$, where $0 \leq x \leq 2$.

15 53. The battery of claim 29, wherein the cathode material has the formula $Li_3Fe_2(PO_4)_3$.

54. The battery of claim 28, wherein the cathode material has the formula $Li_2FeTi(PO_4)_3$.

20 55. The battery of claim 28, wherein the cathode material has the formula $Li_xTiNb(PO_4)_3$, where $0 \leq x \leq 2$.

56. The battery of claim 28, wherein the cathode material has the formula $Li_{1+x}FeNb(PO_4)_3$, $0 \leq x \leq 2$.

25 57. A secondary battery comprising an anode, a cathode and an electrolyte, said cathode comprising a rhombohedral NASICON material having the formula $Y_xM_2(PO_4)_y(XO_4)_{3-y}$, where $0 < y \leq 3$, M is a transition-metal atom, $0 \leq x \leq 5$, Y is Li or Na, and X = Si, As, or S.

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58. The battery of claim 34, wherein said cathode material has the formula $\text{Li}_{1+x}\text{Fe}_2(\text{PO}_4)(\text{SO}_4)_2$, where $0 \leq x \leq 2$.

5 59. A secondary battery comprising an anode, a cathode and an electrolyte, said cathode comprising a rhombohedral NASICON material having the formula $\text{A}_{3-x}\text{V}_2(\text{PO}_4)_3$, where A may be Li, Na or a combination thereof and $0 \leq x \leq 2$.

10 60. The battery of claim 36, wherein the cathode material has the formula $\text{Li}_{2+x}\text{NaV}_2(\text{PO}_4)_3$, where $0 \leq x \leq 2$.

15 61. A variable optical transmission device comprising transparent semi-conductor coated glass or plastic, and including at least one positive electrode and at least one negative electrode separated by a solid or gel electrolyte, wherein at least one electrode comprises a modified olivine compound as set forth in claim 23.